SULPHATE REDUCTION AS A GEOMORPHOLOGICAL AGENT IN TIDAL MARSHES (‘GREAT MARSHES’ AT BARNSTABLE, CAPE COD, USA)

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ABSTRACT

Many tidal marsh surfaces feature water-filled depressions, known as salt pans (shallow) or ponds (deeper). In the great Marshes at Barnstable, Cape Cod, pond formation is an active process. We hypothesize that degradation of organic matter by sulphate-reducing bacteria in these peat-rich marsh deposits is the primary cause of pan and pond formation. Sulphate reduction below an actively developing pond is probably enhanced by higher temperature and salinity of the pond water. Computer simulation suggests that ponds with similar characteristics to those in the Barnstable marshes may develop by sulphate reduction. Necessary conditions are sufficiently deep percolation and diffusion of sulphate into the underlying marsh deposits, and a high decomposition rate stimulated by high water temperatures in the ponds. In areas with a high density of ponds, drainage of the ponds by headward erosion of tidal creeks may cause rapid disintegration of the marsh surface. © 1998 John Wiley & Sons, Ltd.

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KEY WORDS: salt pans; salt marsh ponds; salt marsh geomorphology; sulphate reduction; peat degradation modelling

INTRODUCTION

Vegetation dynamics and physical processes of sedimentation and erosion shape the typical creek pattern of salt marshes. Besides creeks, many tidal marsh surfaces along the coasts of western Europe and North America show numerous water-filled depressions, known as salt pans (shallow) or ponds (deeper). Several explanations have been advanced for the genesis of these depressions (Verger, 1968).

Excluding depressions of anthropogenic origin (duck ponds, peat diggings, etc.), pans and ponds may be of primary or secondary origin (Verger, 1968). Primary pans are supposed to originate from the incomplete colonization of mudflat surfaces by vegetation (Yapp *et al.*, 1917, cited by Verger, 1968). Once an isolated bare patch has been established, it persists because frequent occurrence of standing water and/or high salinity results in adverse conditions for vegetation growth. Ultimately a depression may form, because of the lower sedimentation rate compared with that of the surrounding marsh vegetation. Redfield (1972) describes the occurrence of this process in the ‘Great Marshes’ at Barnstable.

Secondary pans originate after the establishment of a high marsh surface (defined as a vegetated marsh surface above local mean high water). Pethick (1974) has shown for some British marshes that older marsh surfaces display a higher density of pans. Consequently, at least some of these pans originated after a high marsh surface was established and must be of the secondary type. Formation processes for secondary pans mentioned by Verger (1968) are creek blocking and disturbance of the vegetation mat and subsequent deepening by erosion. Dionne (1989) describes pan formation by ice-scouring in cold-climate marshes. Redfield (1972) attributes secondary pond formation to decay of the surface layer of the marsh peat.

Recent observations demonstrate that in many marshes, pans and ponds are actively growing. This process contributes significantly to marsh degradation, since areas with a high pond or pan density are prone to creek and wave erosion (Stevenson *et al.*, 1985; Pye and French, 1993; Downs *et al.*, 1994; DeLaune *et al.*, 1994).

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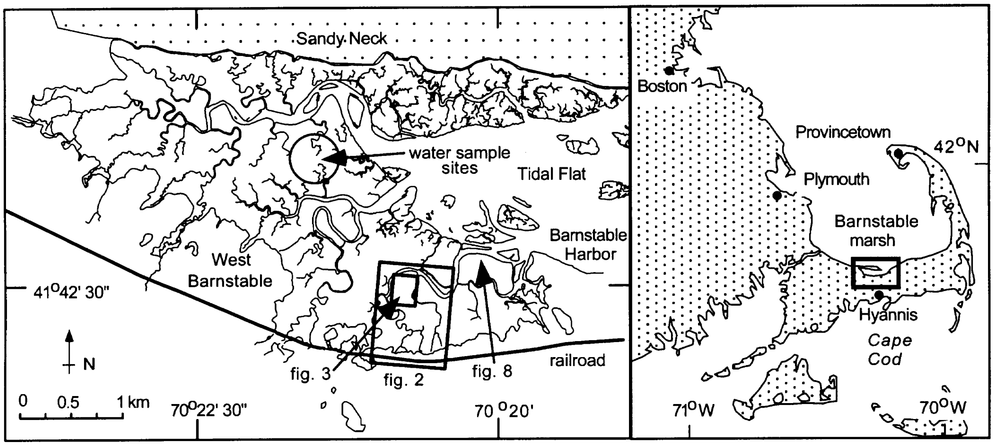

Figure 1. Location of the study area. Left: the Barnstable marshes with creek pattern and location of Figures 2, 3 and 8, and water sampling sites of Table II. Right: map of Cape Cod (Massachussets, USA), showing location of the Barnstable marshes

Table I. Organic matter content of five marsh sediment samples, Banstable marshes.

Location	Loss on ignition (%)	Porosity (%)	Dry bulk density ($g\,cm^{-3}$)	Organic C content (%)	Organic C content ($mmol\,l^{-1}$)
Bank of pan	37·6	92·9	0·25	19·13	3937
Marsh surface, short *Spartina alterniflora*	34·5	85·7	0·31	16·56	4240
Bare patch	32·3	87·7	0·28	15·32	3551
Bare patch	27·3	83·9	0·30	13·26	3308
Bank of creek	18·4	82·7	0·40	8·26	2774

Loss on ignition is the weight loss of the dry sample after combustion at 550°C. Total carbon content has been determined using a Carlo Erba Na 1500 combustion-gas chromatography autoanalyser. Organic carbon content has been derived by applying a correction for carbonate. Porosity is derived by dry-weighing fixed volumes of sediment and determination of solids density using a Micromeritics Accupyc 1330 helium pycnometer.

Therefore, an understanding of the genesis of pans and ponds and how this affects marsh erosion is important in explaining the erosional degradation of marshes. The thesis of this paper is that biogeochemical processes play a key role in the origin of pans and ponds, and therefore contributes to the overall geomorphology of marshes with a significant organic component in the sediment.

THE STUDY AREA

We studied pond formation and marsh erosion in the Great Marshes at Barnstable, Cape Cod, Massachussets (Figure 1), as part of a study on marsh stratigraphy and sea-level rise. The area experiences a humid continental climate. Long-term meteorological records from nearby Hyannis (1951–1991 for temperature and 1896–1991 for precipitation) give mean annual winter and summer temperatures of 0°C and 21°C respectively, and an average annual precipitation value of 1096 mm, with a non-distinct dry season during June and July (Schellekens, 1994; Redfield, 1972). The tide is semi-diurnal with an average range of 3 m. Over 90 per cent of the water volume is replaced every tide at peak flow velocities of more than $0{\cdot}5\,m\,s^{-1}$ (Redfield, 1972; Van der Molen, 1997). At high tides, the salinity of the water in the creeks of the Great Marshes measures around 28 promille (Ayers, 1959). Depending on the influence of seepage, precipitation and evaporation, shallow pore-water salinity may vary over a range of 2·5 to 35 promille (De Rijk, 1995).

Two main vegetation zones can be discerned in the marshes. The low marsh zone occurs between approximately mean sea-level and mean high water level, and is vegetated exclusively by tall *Spartina alterniflora* (height 1–1·5m). The high marsh zone is found above mean high water level (MHW), and is not reached by every tide (Redfield, 1972). This zone supports a more varied vegetation. Well-drained sites near creeks are dominated by several grass species, mainly *Spartina patens* and *Distichlis spicata*, whilst the

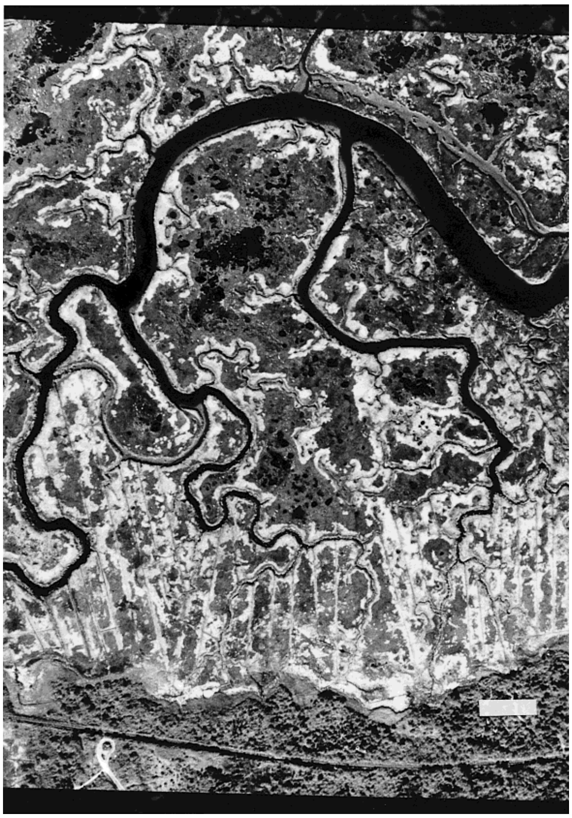

Figure 2. Detail of high altitude colour infrared photograph of a high marsh area in the Barnstable marshes. See Figure 1 for location. Light zones along creeks: well-drained marsh surface with *Spartina patens* and high *Spartina alterniflora* vegetation. Slightly darker areas: poorly drained marsh surface with stunted *Spartina alterniflora* vegetation. Darkest areas are ponds; some drained ponds show up lighter. The straight light lines approximately perpendicular to marsh edge are drainage ditches. Scale bar: 100 m

waterlogged inter-creek areas carry a uniform vegetation of ‘stunted’ *Spartina alterniflora*, a dwarfed form of much smaller size (5–15 cm). Hydrogen sulphide production, promoted by anaerobic soil conditions, probably inhibits the growth of taller *Sp. alterniflora* at these sites (Howes *et al*., 1981; Koch *et al*., 1990).

The high marsh deposits at Barnstable consist of clayey peat, largely composed of the roots and rhizomes of marsh grasses. Organic matter content of this sediment may be as high as 38 per cent (Table I). Low marsh deposits and sediments close to creek banks consist of clay, silt or fine sand with *Spartina* rhizomes (Redfield, 1972). Creeks crossing the high marsh areas have steep, subvertical banks. Besides creeks, many shallow salt pans and deeper ponds occupy the high marsh areas above the mean high tide level. These ponds contain standing water up to 1 m deep and have diameters up to 30 m (Figures 2 and 3). The banks of the ponds often appear to be overhanging (Figure 4). Most ponds contain a layer of clayey mud of very low consistency overlying more cohesive older peat or clay. The ponds occur most frequently in ill-drained inter-creek areas dominated by stunted *Spartina alterniflora*.

Comparison of air photos from different years shows that ponds are actively forming and enlarging in the high marsh areas of the Barnstable marshes (Polissar and Pack, 1993; Reid, pers. comm.; this study). Thus pond formation, which is the subject of this paper, is a highly significant process in these marshes.

SALT PAN AND POND FORMATION

Most ponds in the high marsh zone of the Barnstable marshes are of secondary origin. Comparison of air photos of 1968 and 1992 show that at least some of the ponds are younger than the high marsh surface and that their formation and growth is an active process (Figure 3). Moreover, cores taken from the pond bottoms and surrounding marsh show that the high marsh ponds are virtually never underlain by low marsh deposits, but by

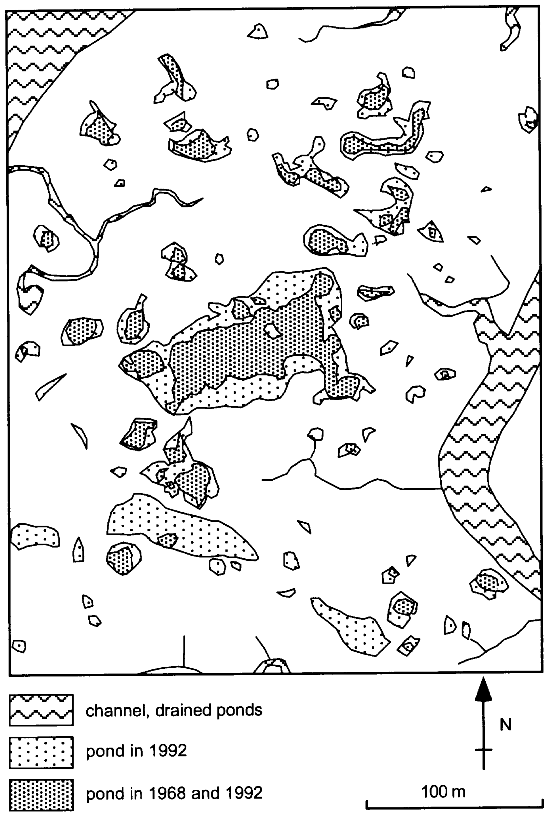

Figure 3. Pond growth between 1968 and 1992. Pond areas have been established by comparing panchromatic air photos dating from 1968, and colour infrared photography of 1992. Overlay of interpreted air photos was accomplished using GRASS GIS. See Figures 1 and 2 for location

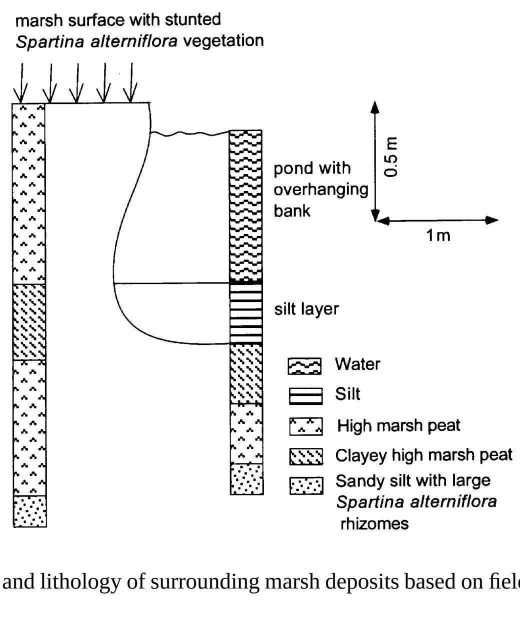

Figure 4. Pond cross-section and lithology of surrounding marsh deposits based on field observations and boreholes

the same type of high marsh peat that surrounds them (Figure 4). Primary pans do occur in the Barnstable marshes. Redfield (1972), who studied these marshes extensively, describes how with increasing elevation of the evolving marsh, the number of depressions decreases until only scattered primary pondholes remain when the marsh has grown up to MHW. Therefore primary ponds may be rare on the high marsh surface. Because of the highly dynamic low marsh environment only few of these pans are likely to persist until a high marsh reaching above MHW has been established. The low marsh ponds are flooded at every tide, which prevents hypersaline conditions and provides a regular input of fresh sediment. They are likely to be colonized by high *Spartina alterniflora* vegetation within a short time.

At this stage it is useful to distinguish between initiation of a secondary pan and its subsequent lateral extension and deepening into ponds. Several processes may be involved in the initiation of a salt pan.

1. Local vegetation is destroyed by suffocation under plant debris or mats of algae (Verger, 1968; Pethick, 1974). Although recolonization of bare patches may result in a *Spartina* vegetation again within three years (Bertness and Ellison, 1987), the dwarf *Spartina alterniflora* vegetation in the inter-creek areas in the Barnstable marshes may be more sensitive to disturbance than the better drained *Spartina patens* sites described by these authors.
2. 'Vegetation dieback' as described by Pye and French (1993), is caused by phytotoxic sulphide or salt levels in marsh soil.
3. Ice-rafting of blocks of marsh vegetation and peat occurs in winter (Dionne, 1989). Ice-rafted peat blocks have been observed on the Barnstable marshes; these blocks may attain a considerable size (4×5 m).
4. The vegetation mat is disturbed by anthropogenic processes. For instance, walking tracks in the Barnstable marshes tend to develop into standing-water areas.
5. Damming of creeks by blocks of peat slumping into the creek may create deeper ponds. However, the plan form and spatial arrangement of the ponds in the Barnstable marshes do not suggest that this process is of frequent occurrence (Figure 2). Blocks slumped into creeks have been observed, but these tend to be eroded rapidly by ebb currents.

Although several processes may initiate pans, their further evolution into ponds is less clear. In particular, the depth of ponds in the Barnstable marshes is difficult to explain. The average pond depth measured at 38 sites is 62·4 cm, with a maximum of 135 cm. Deepening of the ponds may be important for lateral extension as well, since pond widening may involve erosion of the pond banks by wave action and the subsequent storage of the eroded bank material on the pond bottom.

One possible mechanism for deepending of pans is the occurrence of a sedimentation lag between the pond site and its surroundings. Organic and inorganic sedimentation may be lower at unvegetated sites, where organic sedimentation is lacking and less sediment is trapped between vegetation. This is unlikely to be the only mechanism in the case of the deeper ponds, however. Mean sedimentation rate is assumed to equal the rate of sea level rise (Redfield and Rubin, 1962; Middelburg *et al.*, 1996). With a sedimentation rate of 1 mm a^{-1} during the last 1000 years, the formation of a pond with a depth of 1 m would take at least 1000 years. Even taking into account the recent sea-level rise (2·5 mm a^{-1} during the last 80 years; Middelburg *et al.*, 1996) it would still require 400 years. The persistence of a pond at the same location for such a long time is unlikely in the dynamic marsh system, because it may be recolonized by vegetation in its early stages of formation (Bertness and Ellison, 1987) or is likely to be drained by eroding creeks. Deepending of ponds by erosion during storm tides may occur (Stevenson *et al.*, 1985; Pye and French 1993; Reed, 1991). However, it is doubtful whether the cohesive peat underlying most ponds may be eroded deeply. The air photo comparison (Figure 2) indicates that ponds form an order of magnitude faster (tens of years) than the time spans indicated above (hundreds of years).

The mechanisms outlined above insuffificently explain the depth and rapid growth of ponds in the Barnstable marshes. Redfield (1972) noted the decay of surface turf ('rotten spots') in small areas where the grass had died, resulting in the formation of irregularly shaped pond holes. He attributed these phenomena primarily to decay of the surface layer of the marsh peat. The death of the vegetation and subsequent decomposition of the underlying peat he explained as the result of inadequate drainage and concentration of salt by evaporation. According to our own observations, many ponds in the Barnstable marshes show visual indications of decomposition of the peat: loose peat fragments, and crumbly, ragged fringes.

Based on these observations, we hypothesize that biochemical decomposition of the organic matter in the marsh sediment is the most important process in pond deepening and areal growth. In particular, anaerobic decomposition may be an explanation for the depth of many ponds in the Barnstable marshes. Aerobic decomposition of marsh peat is likely to be effective only near the waterline of the pond, and thus may contribute to its areal growth, but anaerobic decomposition may be effective also at the pond bottom, provided favourable conditions are present. Besides causing direct loss of organic matter, decomposition also may decrease the cohesion of the peat by reducing the mechanical strength of plant tissues and consequently reducing its resistance to erosion.

Anerobic decomposition of organic matter is based on different microbial metabolic processes: nitrate reduction, manganese and iron reduction, sulphate reduction and methanogenesis, occurring at successively lower redox potentials (Reddy *et al*., 1986). In general, these are slow processes, compared to aerobic degradation. In salt marsh sediments, sulphate reduction and methanogenesis are the most important processes (Howarth and Teal, 1979; Howes *et al*., 1981). In sediments, methanogenesis does not occur before sulphate has been depleted because of a competitive advantage of sulphate-reducing bacteria with respect to methane producers (Jørgensen, 1984). Methanogenesis in marine sediments occurs below the upper zone of sulphate reduction, generally at a lower rate than sulphate reduction.

Because of the abundant supply of sulphate-rich water, the degradation of organic matter by sulphate-reducing bacteria is the most likely anaerobic decomposition process at the bottom of the ponds, and may account for most of the deepening of the ponds. Sulphate reduction of organic matter is the result of the metabolic process of obligate anaerobic bacteria (e.g. Reddy *et al*., 1986). The generalized reaction equation is:

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \quad (1)$$

When H_2S diffuses upward into higher sediment or water zones, it is oxidized again upon contact with oxygen, or used by green and purple phototrophic sulphur bacteria to assimilate CO_2.

Sulphate reduction in salt marsh deposits has been described by several authors (e.g. Howarth and Teal, 1981; Lord and Church, 1983; Howes *et al*., 1984; Casey and Lasaga, 1987; King, 1988). Very high sulphate reduction rates have been reported from salt marshes: 86 mol C m^{-2} a^{-1} in a Cape Cod salt marsh (Howarth and Teal, 1979), although this may be overestimated (Howes *et al*., 1984; King, 1988). The latter authors report sulphate reduction rates of 33–36 mol C m^{-2} a^{-1}. The highest sulphate reduction rates have been reported from dwarfed *Spartina alterniflora* stands, which in the Barnstable marshes are the sites with the highest density of ponds.

Evidence of high sulphide production below the ponds is shown by the high amount of gaseous H_2S released upon disturbance of the bottom sediment, and the whitish, yellowish or reddish-brown and purple colours in the water or between algae, that may indicate the presence of sulphide oxidizing bacteria. Water chemistry samples from the ponds collected during the summer of 1995 confirm the importance of sulphate reduction, although direct measurement of sulphide production failed. The samples have been collected during a prolonged period of dry and hot weather and low spring tides. The high Cl concentration relative to creek water indicates concentration of the pond water by evaporation (Table II). However, the sulphate concentration is lower than might be expected (based on the concentration factor computed from the Cl concentration), which indicates removal of sulphate from the pond water (Table II).

Since anaerobic decomposition occurs throughout the marsh sediment, special conditions may occur in the ponds that enhance organic matter decomposition with respect to the surrounding marsh peat. Under normal conditions, degradation of organic matter is balanced by the organic production of vegetation at the marsh surface. Sulphate reduction occurs throughout the marsh sediment up to a depth where consumption of sulphate balances transport of sulphate into the sediment by diffusion and downward percolation of water (Appelo and Postma, 1993; Lord and Church, 1983; Casey and Lasaga, 1987). In poorly drained *Spartina* marshes, most of the degradation occurs within a zone of 25 cm below the surface, where it accounts for the breakdown of freshly produced root matter (Howarth and Teal, 1979).

We assume that the presence of a layer of standing water, in which sulphate tends to be concentrated by evaporation, represents the special conditions necessary for enhanced sulphate reduction at the sites of pan formation. A higher sulphate concentration at the surface will cause more rapid and deeper diffusion of sulphate

Table II. Water chemistry and depth data of ponds.

	pH (field)	Cl ($mmol\,l^{-1}$)	SO_4 ($mmol\,l^{-1}$)	Concentration factor	SO_4 deficit ($mmol\,l^{-1}$)	Depth of pond (cm)	Thickness mud (cm)
Average all ponds	7·52	467·2	24·75	1·23	0·90	62·4	31·6
Average 'inactive' ponds	7·72	457·8	24·43	1·21	0·71	89·8	45·8
Standard deviation	0·68	37·7	1·87	0·10	0·96	22·2	42·1
Average 'active' ponds	7·34	476·5	25·08	1·26	1·08	32·1	18·5
Standard deviation	0·46	51·2	1·90	0·14	1·31	10·2	34·9
Significance 10%						significant	significant

Distinction has been made between ponds with and without phenomena of active sulphide oxidation near the water surface ('active' and 'inactive' ponds, see text). Each of both groups consist of 10 ponds in two pond complexes. Concentration factor and SO_4 deficit have been calculated on the basis of Cl and SO_4 concentration in a nearby creek ($Cl = 377\ mmol\,l^{-1}$ and $SO_4 = 20{\cdot}7\ mmol\,l^{-1}$). Depth has been measured at 38 locations (20 inactive, 18 active ponds). Thickness of mud layer has been measured at 25 locations (12 inactive, 13 active ponds). Significance test with Students' *t*-test, significance level 10%

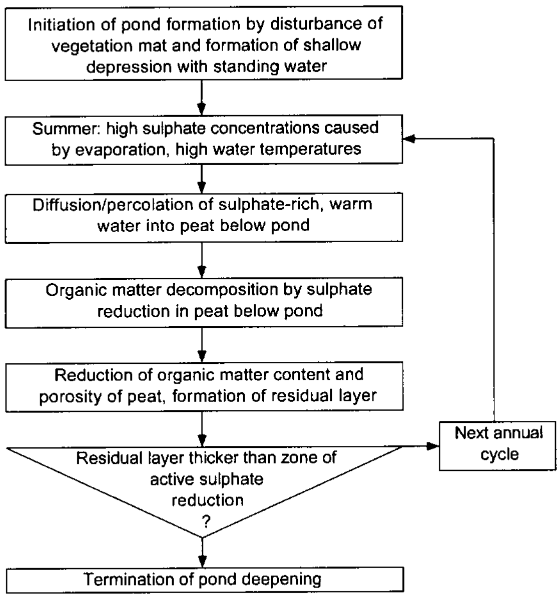

Figure 5. Flow chart of the pond growth process as modelled by computer simulation

into the underlying sediment, exposing a thick layer of organic matter to decomposition. Moreover, a pan is almost constantly filled with water, providing a prolonged source of sulphate, while the normal marsh surface may not be flooded for weeks. By contrast to the surrounding marsh surface, organic productivity is negligible at the pan sites as conditions are adverse for plant growth (high and variable salinity, sulphide toxicity, presence of standing water inhibiting growth of *Spartina*).

A SIMULATION MODEL OF POND FORMATION BY SULPHATE REDUCTION

To test whether bacterial sulphate reduction could produce deep ponds within a time span of tens of years, and to assess which parameters may have a strong influence on the process, a computer simulation model has been constructed (Figure 5).

It is assumed that as a result of the initiation of a pan, sulphate-rich water is introduced into the peat below the pan which locally enhances or reactivates sulphate reduction. Furthermore, it is assumed that reduction rate is

equal throughout this active sulphate reduction layer. The rate of sulphate reduction primarily depends on organic matter concentration and is represented by a first-order rate law:

$$\mathrm{d}G/\mathrm{d}t = -\mathrm{k}G \tag{2}$$

in which G is organic matter concentration (e.g. Berner, 1964; Reddy *et al*., 1986). The constant k depends on the type of organic matter. Experiments by Westrich and Berner (1984) show that fresh organic matter degrades at higher rates than partly decomposed organic matter. This can be accounted for by assuming different k values for separate organic matter fractions (Multi-G model; Westrich and Berner, 1984). Since the most labile organic matter is consumed first, the result is a k value decreasing with time. Middelburg (1989) therefore has formulated an alternative model in which k decreases logarithmically with time (power model). Furthermore, the rate of sulphate reduction depends exponentially on absolute temperature (Abdollahi and Nedwell, 1979). For a first simple approach, k is assumed to be constant in the model calculations.

In the model, the simple G model of Berner (1964) is used, since the most labile organic matter is assumed to have been removed already during deposition of the peat. The decomposition of a layer of peat by sulphate reduction results in a new layer with a lower organic matter content. However, porosity shows a strong positive correlation with organic matter content in peaty marsh sediments (Table I; Bradley and Morris, 1990). Therefore, the removal of organic matter also causes a reduction of porosity and, consequently, the volume of the layer. As a result, most of the volume reduction is achieved indirectly, by the reduction in porosity due to loss of organic matter, rather than by the reduction of the volume of organic matter itself. This reduction in porosity by the decomposition of peat may be caused by collapse of pore-supporting organic matter. DeLaune *et al*. (1994) present field evidence of porosity reduction ('peat collapse') as a cause for ponding in a Louisiana coastal marsh.

The one-dimensional model computes the reduction in volume due to sulphate reduction and consequent porosity collapse of a column of sediment with unit base area. It is assumed that sulphate reduction is active only during part of the year, when temperatures are sufficiently high. The model repeats a number of yearly cycles. Each year, a certain amount of organic matter is reduced from a layer of thickness D at the bottom of the pond, using reduction rates computed with Equation 2. During each cycle, a residual layer with a lower organic matter content and porosity is produced. A linear relation between porosity and organic matter content is assumed. Before the new reduction cycle starts, the residual layer is 'mixed' with the peat below, to produce a new layer of thickness D with average organic matter content and porosity. This layer is subjected to the next reduction cycle. Although it is not likely that in reality mixing of old marsh peat and residue occurs at the pond bottom, mixing is assumed in the computer model for computational efficiency. The result is not strongly influenced by this procedure. The process is stopped when the organic carbon content of the residual layer (after mixing) is less than 2 per cent of that of the original peat. In that case, the thickness of the residual layer practically equals D.

We tested the influence of three parameters: the k parameter in Equation 2, the thickness (D) of the layer with active sulphate reduction below the evolving ponds, and the sediment organic matter content (O). Data for adding reliable parameters to a computation of D using a diffusion equation are still lacking; therefore the model was tested with several fixed thicknesses for the active sulphate reduction layer. Sedimentation rate is assumed to be a constant amount of $0{\cdot}1\,\mathrm{mm\,a^{-1}}$ of organic matter, and $0{\cdot}1\,\mathrm{mm\,a^{-1}}$ of mineral matter.

Model runs have been made using the following combinations of parameters:

1. fixed values for k (Equation 2) and organic matter content O, variable thickness of the layer with active sulphate reduction D;
2. fixed D and O, variable values of k;
3. fixed D and k, variable organic matter content O.

The actual value of k for the conditions in the Barnstable marshes is unknown. Reduction rates have been published for different marsh sediments (e.g. Lord and Church, 1983), but data on the value of k are lacking. Literature data on the actual value of k usually pertain to deep-water sediments with planktonic organic matter instead of peat deposits. Westrich and Berner (1984) determined values of $7{\cdot}2$ and $8{\cdot}8\,\mathrm{a^{-1}}$ for fresh plankton, and $0{\cdot}84$ and $1{\cdot}02\,\mathrm{a^{-1}}$ for plankton degraded by oxidation. The latter value range may apply for marsh peat as well,

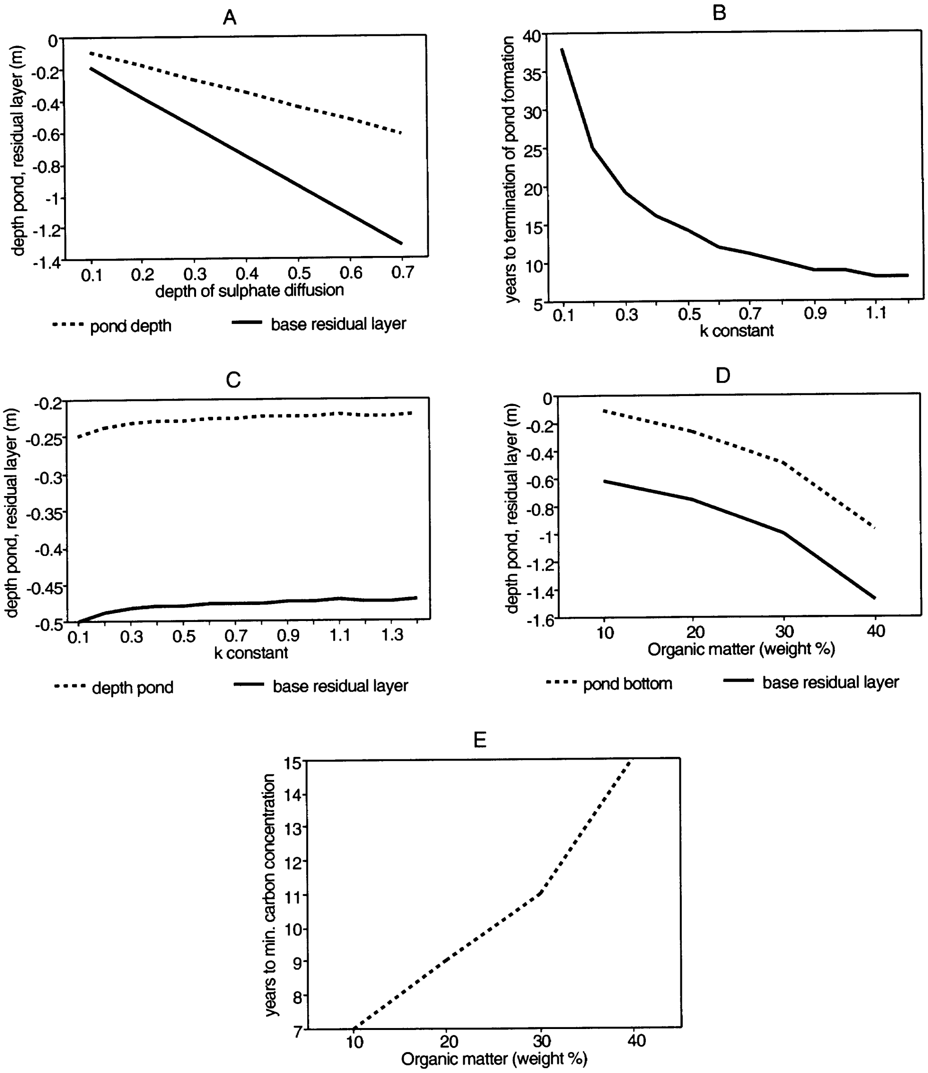

Figure 6. Results of computer simulation of pond growth. (A) Influence of thickness *D* of layer with sulphate reduction on pond and residual layer depth. (B) Influence of k constant in Equation 2 on rate of pond deepening. (C) Influence of k constant on pond depth. (D) Influence of substrate organic matter content on pond depth. (E) Influence of substrate organic matter content on rate of pond deepening

since the peat underlying the ponds has already undergone a decomposition phase immediately after its deposition. Lord and Church (1983) computed a value of 0·04 a^{-1} from modelling of sulphate profiles under stunted *Spartina alterniflora* stands.

Sediment parameters have been derived from laboratory measurements on marsh peat samples (Table I). Porosity and dry bulk density correlate well with the organic matter content. This correlation is used to estimate these parameters for model runs with varying sediments. To calculate the new porosity of the sediment from the organic matter content after each reduction step, the following relation has been used:

$$P = 73{\cdot}35 + 0{\cdot}44O \tag{3}$$

in which *P* is porosity and *O* is organic matter content.

Realistic values for the thickness of *D* of the layer with active sulphate reduction can be obtained from data on sulphate reduction below regular marsh surfaces. Howarth and Teal (1979) show that most sulphate reduction occurs in the first 25 cm below the marsh surface. King (1988) published a sulphate reduction rate

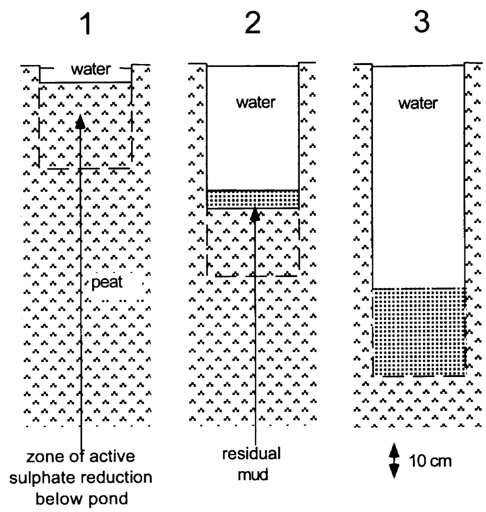

Figure 7. Retardation and final termination of pond growth by development of residual mud layer. (1) Initial pond without mud layer; all sulphate reduction occurs within the peat substrate. (2) Residual mud layer has formed; part of sulphate reduction occurs within this layer, in which organic matter content is gradually reduced by decomposition. (3) Residual layer has grown thicker; nearly all sulphate reduction occurs within this layer. Further peat decomposition has ceased

profile with low values already within the first 10 cm. Yearly fluctuations in sulphate concentration may extend down to 30 cm below a salt pan (Casey and Lasaga, 1987). Values for D below the ponds may be higher than those at the marsh surface, since the sulphate concentration in the pond water may be higher than that of the normal flood water at the marsh surface.

A number of model runs indicate the influence of the different parameters on the duration of pond formation and the resulting pond depth. The pond depth and the ultimate thickness of the residual layer are linearly related to the thickness of the sulphate reduction layer D (Figure 6A). After several cycles, all sulphate reduction occurs within the residual layer, and consumption of the underlying peat is effectively stopped. Pond deepening then continues slowly until the organic matter of the residual layer is consumed, suggesting that a maximum depth exists at which further deepening is halted (Figure 7). Under field conditions, the formation of a residual layer with lower porosity is likely to retard further sulphate diffusion and percolation into the underlying peat.

As expected, the k parameter of Equation 2 exerts most influence on the rate of pond formation, which is expressed as the number of years in which the maximum depth has been reached (Figure 6B). In reality, the final stage of pond deepening, when most of the organic matter consumption occurs within the residual layer, is expected to proceed more slowly than indicated by the model, since sulphate reduction rate slows down with time (Middelburg, 1989). The value of k does not influence the ultimate pond depth (Figure 6C).

The type of sediment determines both the ultimate depth of the ponds and the duration of their formation (Figure 6D,E). Ponds develop more slowly and grow deeper in sediments with a high organic matter content. The thickness of the residual layer is the same for all types of sediment, and is determined by the thickness of the layer with active sulphate reduction. This is, however, the consequence of fixing D irrespective of the sediment properties instead of computing it using sediment porosity data. Under field conditions the rate of diffusion and percolation of sulphate depends on porosity (Appelo and Postma, 1993). As a result, the residual layer will be thicker in sediments with a high organic matter content, since porosity is positively correlated with organic matter content.

DISCUSSION

The simulation model for pond formation needs further refinement, especially with respect to calculation of sulphate concentration profiles in the sediment. However, the simulation results show that locally enhanced sulphate reduction is a viable hypothesis to explain the formation of ponds. Many ponds contain a layer of silty

mud with a low organic matter content (Figure 4) that may be interpreted as a residue of the decomposed peat. Further research into the properties of this mud may confirm this origin. Also, the depth of the simulated ponds agrees with that found in the field.

The model results suggest that decomposition of peat at the pond bottom continues until a residual layer has been formed that is thicker than the depth of sulphate diffusion (Figure 7). Consequently, after a number of years of active growth, further deepening of the pond by sulphate reduction is halted. This implies that in the marsh, actively growing ponds may be present, together with older ponds lacking indications for highly active sulphate reduction. Visual inspection combined with water chemistry suggest that this distinction can indeed be made. Many ponds have clear surface water, contrasting with ponds that exhibit the above-mentioned signs of high sulphide production: whitish, turbid water or reddish and purple colours, probably caused by the presence of coloured sulphur bacteria. This difference corresponds with a different water chemistry (Table II). The clear ponds, which are deeper on average, show a lower concentration factor, lower pH, and a smaller deficit in sulphate concentration (Table II). It is likely that the deeper ponds have reached a depth at which active sulphate reduction is halted.

The k values (Equation 2) necessary for pond development appear to be higher than those cited in the literature, since air photo studies suggest that ponds may develop within a time span of less than 20 years (Figure 6). Values of k may therefore be higher at the pond sites than the value of $0{\cdot}04\,a^{-1}$ found by Lord and Church (1983). A possible explanation is the temperature of the pond water, which may be warmer than the interstitial water at comparable depths in the surrounding peat. Sulphate reduction is enhanced strongly by higher temperatures, producing higher k values (Abdollahi and Nedwell, 1979; Westrich and Berner, 1984). Temperature measurements in marsh peat at Barnstable show a mean temperature slightly above 10°C with an annual amplitude of ±6°C near the surface (Redfield, 1964). The annual amplitude will be higher in the standing water of the ponds (Nedwell and Abram, 1979). During the summer of 1995, average water temperatures measured 33·5°C, with a maximum of 43·9°C. These temperatures approximate the optimum value for sulphate reduction for common genera of sulphate-reducing bacteria (Abdollahi and Nedwell, 1979). Near the top of the water column, temperatures are significantly higher than in the peat soil surrounding the ponds (36·2 versus 33·4°C), whilst at deeper levels differences become smaller. At 1 m depth below the water surface, temperature still averages 30·1°C, with a maximum of 42°C. In combination with a much higher sulphate supply rate, this should significantly enhance sulphate reduction at the bottom of ponds with respect to the surrounding marsh peat. However, since these temperature measurements have been made during a prolonged period of dry and warm weather, more continuous records should be collected to confirm this effect.

Our assumption, that evaporation enlarges the depth of sulphate diffusion below standing water and creates favourable conditions for pond growth, cannot be confirmed by the model since the sulphate penetration depth D is prescribed to the model. However, the model confirms that high D values are favourable for development of deep ponds, of similar depth to those in the Barnstable marshes. The development of a layer of standing water in which sulphate may be concentrated may therefore be critical for pond initiation and growth. Several processes for initiation of ponds have been listed above, all of which may create an initial layer of water leading to locally enhanced sulphate reduction.

Near creeks, vertical advective flow from flood water through the marsh peat may cause deeper sulphate penetration (Hemond *et al.*, 1984; Nuttle, 1988). This suggests that headward erosion of creeks into high marsh areas may enhance pond formation by amplification of vertical water-table movements and advection of sulphate-rich water.

If sulphate reduction is a valid explanation for the process of pond formation in the Barnstable marshes, this process should contribute to pond formation in other areas as well. The model indicates that the deepening of the ponds is caused by a combination of decomposition of the peat itself, and a reduction in porosity in the residual material. This agrees with the observations of DeLaune *et al*. (1994), who attribute ponding to porosity collapse of the peat. Sulphate reduction may provide the necessary loss of structural stability of the peat matrix.

As the simulation model shows, sediment organic matter content strongly influences the ultimate depth of the ponds. Pond depth is almost negligible at organic matter contents lower than 10 per cent. However, pans do occur in marshes with sediments at lower organic matter content than the Barnstable marshes, for instance in marshes at the head of the Bay of Fundy in Canada (Dekker and Van Huissteden, 1982) and in marshes along

Figure 8. Pond, drained by headward erosion of a small creek. Arrow: remnant of subsoil pipe through which the creek and the pond made first contact. Note the overhanging bank of the former pond.

European coasts, as described by Verger (1968) and Pethick (1974). In the Bay of Fundy marshes, the morphology of the pans is similar to that of the ponds in the Barnstable marshes, but the depth and size of the pans are generally smaller, as predicted by the model for sediments with lower organic matter content. Possibly, erosion during storm tides may play a greater role in these cases, producing pans by removal of sediment in combination with sulphate reduction. The role of sulphate reduction then would be mainly the decomposition of fibrous organic matter that otherwise protects the sediment from erosion.

We consider pond formation an important process in the sedimentation–erosion cycle in salt marshes. In this respect, three processes deserve further attention in future research: the present rate of pond growth compared with previous rates; the lateral growth of ponds; and the rapid erosion of the marsh surface that may occur when pond complexes are drained by creeks.

The rapid rate of pond growth as determined from air photos suggests that pond formation may have been enhanced in recent years in the Barnstable marshes. To confirm this, a comparison of air photos of different dates from wider areas of the marshes is necessary. A study of a large number of cores taken from the marsh sediments shows only a few cores with sediments that may be interpreted as pond bottom mud (Lubberts, pers. comm. 1995; in prep.). Large-scale preservation of this type of sediment is, however, not very likely since densely ponded areas are prone to severe erosion (see below). If pond formation has accelerated in recent years, an understanding of the cause is very important for proper management of these marshes. A relation to increased sea-level rise may exist, since increased flooding frequency will influence processes by which ponds are initiated (wrack formation, ice-rafting, and a general increase of ponded water in high marsh areas). Also, human disturbance of the high marsh vegetation mat may not be insignificant.

Lateral growth of ponds is a very active process. Ponds in the Barnstable marshes tend to coalesce into larger complexes, ultimately developing into small lakes (Figures 2 and 3). Wave erosion of the pond banks is a likely process. Wave erosion of peat in the Mississippi delta marshes results in the formation of lakes (Reed, 1991). However, wave erosion may not be the only process since it produces organic debris that would lead to a gradual infilling of the ponds. Decomposition of organic matter is also an important factor in lateral growth: passively, by deepening the ponds and providing storage space for eroded organic matter from the banks, and actively, by the decomposition of eroded organic matter. The banks may also be attacked directly by biochemical decomposition, such as aerobic oxidation of the peat near the water line and sulphate reduction at deeper levels. Many ponds show overhanging banks (Figures 4 and 8). These are not produced by vegetation growing from the sides into the pond water, since *Spartina* shoots have not been observed to grow into the water. Apparently, peat degradation well below the water table contributes to the lateral extension of the ponds.

When headward erosion of a creek reaches a pond, it will be drained, leaving a steep-walled depression in the marsh surface with an unvegetated cover of mud (Figure 8). Subsoil piping, possibly initiated by crab burrows, may accomplish the first contact between the pond and the creek. This is shown by remnants of tunnels in many cases (Figure 8). Where large, interconnected complexes of ponds exist, erosional tapping of ponds probably proceeds rapidly. The resulting areas consist of highly irregular terrain, consisting of many drained ponds, creeks and isolated blocks of peat. Wave attack may further destroy the peat remnants. By this process, larger high marsh areas may be converted rapidly into low marsh and mudflat. In particular, pond complexes near larger creeks appear to be vulnerable to extensive erosion because of the stronger effects of tidal currents and wave erosion. Air photos show that in marsh areas distant from large creeks, the effect of pond tapping is less extensive. In such areas erosional effects may be considerably smaller, since the drainage of pond complexes also causes a renewed supply of clastic sediment and re-establishment of a low marsh vegetation, while effects of wave and current action are relatively small.

In conclusion, the computer simulation experiments and field observations support the hypothesis that microbial activity, by means of sulphate reduction, is an important geomorphological agent in salt marshes with organic-rich sediments, causing the creation and enlargement of pans and ponds. To confirm this hypothesis a more focused geochemical study is needed to measure directly rates of sulphate reduction and other decomposition processes under field and laboratory conditions. Specifically, the rather high values for the rate constant k, as predicted by the simulation model, need validation. To determine the effect of temperature on decomposition rates, more thorough measurements of temperature variations within the ponds and the surrounding peat should be made.

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